

Synthesis, Characterization and Optical Properties of II-VI Semiconductor Nanocrystals

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ABSTRACT

Synthesis of II - VI nanocrystals with different concentration, capping agents and time duration tried and their characterization led to the important conclusions. The effect of particle size of the II - VI semiconductor nanocrystals on the PL spectrum has been investigated theoretically and experimentally. Blue shift in the PL spectrum has been observed with decreasing size of the nanocrystals. The effective mass approximation, the quantum confinement effect, Coulomb charge interactions, the surface charge polarization etc. have been taken into account apart from the usual band gap energy to arrive at a theoretical model. The theoretical model is consistent with the experimental results. The broadening of the PL spectrum with reducing size may be attributed to the band edge luminescence and the particle size distribution while the peak are assigned to the recombination of holes at the deep defects and electrons at the shallow traps. In monodisperse nanocrystals no broadening in the PL spectrum was observed while in the case of the polydispersed nanocrystals there was broadening in the PL spectrum with reducing size of the crystals.

Keywords: Optical properties of II-VI Semiconductor, Nanocrystals.

INTRODUCTION

The terms NANO comes from a Greek word which means dwarf or small.

Nowadays it has rocked the academic world. Everywhere We find it used in the literature. We see it as Nanoparticle, Nanocrystal, Nanosemiconductor, Nanopolymer,

Nanoceramic, Nanomedicine, Nanorobots, Nanoscience, Nanotechnology and many more and even commercial uses as Nanocar. The question is why nano has got prominence? Because we are starved of energy and natural resources. We want efficiency to the optimum maximum level. We want everything right from the computers to other machines functioning target specific faster, precisely, accurately and promptly. We desire the entire system right from the mechanical to the biology system working properly and managing them from the atomic level.

In 1959, Physicist Richard Feynman first outlined the theoretical concept of manipulating atoms. He explained that the properties of physics do not deny the possibility of manipulating things atom by atom. He is credited with being the first persons to advance the possibility of molecular assembly. In 1974 TOKYO Science University Professor Norio Taniguchi coined the term for the first time Nanotechnology to describe precession manufacturing of materials at the nanometer level. In 1986, K. Eric Drexler envisioned a future in which machines far smaller than dust particles would construct every object atom by atom. He presented the concept of universal assembler with a molecular arm. This assembler could hold and position atoms in a precise location, which could construct almost everything. Nanotechnology has revolutionized the molecular engineering. In scientific jargon nano means 10^{-9} . Thus a nanometer means, a billionth of a meter. That is ten times diameter of a hydrogen atoms or 1/80000 of the diameter of a human hair. Invention of transistor by John Bardeen, Willion Shockly

and walter Brattain in 1947 laid the foundation of miniaturized devices. Miniaturization enabled to save space by making the various pieces of equipments compact and material(natural resources).Presently semiconductor devices are finding applications right from kitchen appliances to space - craft covering between them a large range of other applications. In 1970, L. Esaki and his collaborators at IBM in USA produced quantum wells of GaAs and AlGaAs by alternately stacking these two materials on atomic scale. In 1980, A.I. Akimov and his collaborators at Ioffe Physical technical Institute in St. Petersburg noticed that during uneven quenching of a glassy material containing CdSe, a variety of colours were observed. It was possible to explain this fact only by assuming that CdSe particles of different sizes were present. These observations followed by the theories put forward by Efros and Efros in USSR gave surge of activities on the investigation of nanoparticles of semiconductors and many other materials. L.E. Brus in USA developed a theory based on effective mass approximation which could qualitatively explain the size dependence of certain properties of semiconductor nanoparticles. Now tight binding approximation modified forms of effective mass approximation etc. are being used to the experimental observation. Brus group also reported that it is possible to obtain semiconductor nanoparticles in colloidal solution or they can be grown in polymer matrix. Presently we have several techniques of synthesing nanoparticles and characterizing them.

We are preparing them by chemical methods. We are focused upon specimens

are CdS, CdSe, ZnS, ZnS:Mn, ZnS:Cu, ZnS:Ag, CdS:Mn. Characterization of specimen are done by UV - VIS absorption, PL measurement, Electroluminescence, XRD, TEM and SEM.

GROWTH TECHNIQUES OF NANOMATERIALS

Atoms and molecules are the essential building blocks of every object. The manner in which things are constructed with these basic units is vitally important to understand their properties and their reciprocal interactions. An efficient control of the synthetic path ways is essential during the preparation of nanobuilding blocks with different sizes and shapes that can lead to the creation of new devices and technologies with improved performances.

TOP-DOWN TECHNIQUE

A bulk material is taken and machined it to modify into desired shaped and product. Example-IC, steps crystal growth, lithography, Etching, Ion-implantation.

BOTTOM TOP TECHNIQUE

This technique is used to build something from basic material. Example – assembling materials from the atoms and molecules. This is non - lithographic approach and not completely proven in manufacturing but has great potential to become alternative to lithographic process. Example - Organometallic precursor (at low temperature) method, Sol - gel technology, Electron deposition, physical and chemical vapour deposition (PVD, CVD), epitaxial growth, layer ablation etc.

We are using organometallic precursor (at low temperature) method as it is not very costly. By this method of synthesis we have prepared CdS nanocrystals of various sizes by a single source organometallic precursor in non-coordinating solvent ethanol.

STEPS

STEP-[I] Solution A was prepared by dissolving 36 mg cadmium Chloride (CdCl_2) and 12 mg thiourea $(\text{NH}_2)_2\text{CS}$ into a 30 ml ethanol ($\text{C}_2\text{H}_5\text{OH}$) in a flask under magnetic stirrer at 60°C for 10 - 15 minutes.

STEP-[II] Solution B was prepared by dissolving 10 mg Sodium Hydroxide (NaOH) in 10 ml ethanol.

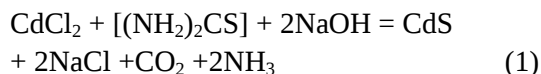
STEP-[III] Solution A and B were mixed and stirred at 60°C . Now nanocrystalline CdS sample is ready in colloidal solution and is taken out 2 ml at different reaction time.

STEP-[IV] The sample takes 24 hrs to settle down in suspension state.

STEP-[V] Nanocrystalline CdS samples are centrifuged for optimum time and CdS nanoparticles are now filtered out.

STEP-[VI] The sample CdS nanocrystals are dried in the sun.

The synthesis mechanism are shown by reaction



To stabilize the nanoparticle size and preventing the nanocrystals from aggregation, capping agent is used. Polymers are good stabilizing agent because they can occupy large surface area of nanocrystals. We use Glucose ($C_6H_{12}O_6$) as a capping agent and found that increasing concentration of capping agent decreases the particle size.

In the preparation of semiconductor nanocrystals the choice of the capping molecules is critical. The bonding between the capping molecules and the precursors needs to be neither too weak nor strong. If the bonding between capping molecule and nanocrystal precursor is too weak, particle growth is fast and bigger crystallites are formed. If the bonding is too strong, the nanocrystals will not be formed. The rate at which the capping molecules attach and de-attach the surface, influences the growth rate and thus the final size of particles. By the choice of the type and concentration of capping molecules and the temperature, the

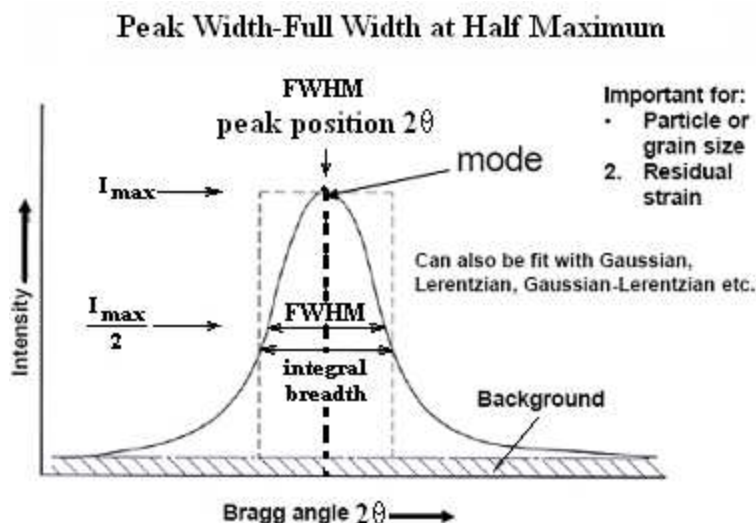
dynamics of attaching and de-attaching can be influenced and the particle size can be tuned. At lower capping molecule concentration, the concentration of the cation capping molecule complex is lower resulting in a faster particle growth. At higher capping molecule concentration the reaction is slower yielding well passivated and more monodisperse particle.

CHARACTERIZATION TECHNIQUES

Characterization of nanomaterials and nanostructures has been based on the surface analysis techniques and conventional characterization methods developed for bulk materials.

FOR SIZE CHARACTERIZATION

The morphological features have been studied through Scanning Electron microscopy (SEM), while their crystal structure has been investigated through X-ray diffraction (XRD) studies.



X- RD STUDIES

X-ray diffraction is a most powerful tool for crystal analysis. X-ray diffraction by crystals gives sharp intense lines because of regular arrangement of atoms. For small crystal sizes, x-ray beam is diffused. This decreases the peak intensity and increases the width of the line. From XRD of nanocrystals one can determine : -a) Crystal structure

- b) Crystallite size and
- c) Lattice parameter

The XRD studies indicate that the nanocrystalline powder and film specimens of CdS are cubic in nature. The broadening

of peaks is indicative of small particle size. The sizes have been computed by using Debye - Scherrer formula, $D = 0.9\lambda/\beta \cos\theta$, where β = FWHM, θ is deviation and D is the size of the nanoparticles. The sizes have been obtained in the range of 2 to 10 nm.

FOR BAND GAP CHARACTERIZATION

The optical studied have been carried out using UV - absorption spectra and Photoluminescence (PL) spectra.

The size of CdS nanoparticles by various techniques are given in the the following table:

Sample name	Reaction time (in min)	Size by TEM (in nm)	Size by XRD (in nm)	Size by absorption edge (in nm)	Absorption edge (in nm)
I	20	6	5.2	5.7	470
II	30	-	-	6.6	480
III	60	8	7.3	8	490
IV	80	10	-	-	-
V	90	-	10.4	10.8	500

ABSORPTION STUDIES

Absorption spectra of powder have shown blue shift in absorption edge as compared to their bulk counterpart indicating increased band gap energy. No effect of doping has been observed on the

absorption spectra. It has been found that as size of nanocrystals decreases, their band gap increases. Absorption result for CdS nanoparticles for various concentration of capping agent are given in the following table:

Sample	Band Gap (e V)	Particle Diameter(nm)
1:0.5	3.88	2.39
1:1	3.5	2.74
1:2	3.3	3.00
1:15	2.6	6.26
TG	3.5	2.74
TGA	2.75	4.57
CYS	3.17	3.23

THEORETICAL STUDIES

The band gap of semiconductor nanocrystal has been calculated using the effective mass approximation (EMA) model (BRUS).

$$E_{g \text{ nano}} = E_g + \frac{\hbar^2 \pi^2}{2R_0^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\epsilon_2 R_0} + \frac{e^2}{R_0} \left(\sum_{n=1}^{\infty} \alpha_n \left(\frac{S}{R_0} \right)^{2n} \right) \quad (2)$$

Where m_e and m_h are the effective mass of electrons and holes respectively, e is the electronic charge, R_0 the radius of the nanoparticles, ϵ_2 the dielectric constant of the nanoparticles, and S is the magnitude of the distance that the wave function peaks from the centre of the spherical particle that is the electron - hole separation, ϵ_1 is the

dielectric constant of the surrounding medium,

$$\epsilon = \epsilon_2 / \epsilon_1, \alpha_n = (\epsilon - 1)(n+1) / \epsilon_2 (\epsilon_n + n+1) \quad (3)$$

I st term is the band gap of the bulk material.

II nd term is the quantum energy of localization for electron and hole

III rd term is the coulomb attraction energy between the electron and hole

IV th term is the mutual polarization energy image of the charges. The bar here represents an average over the wave function.

The theoretical Band Gap for bulk and nanomaterials are given below:

Samples	Band Gap (eV) (Bulk)	Band Gap (eV) (Nano)
CdS	2.42	3.25

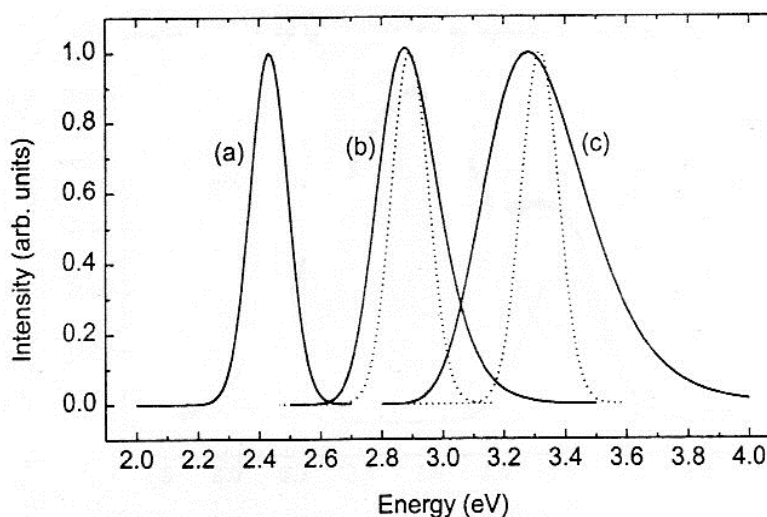


Fig. Calculated photoluminescence spectra of bulk CdS (a), CdS nanoparticles of radius 2.0 nm (b) and 1.5 nm (c). Fullcurves: 14% polydisperse, dotted curves: monodisperse. The peaks exhibit blue shifts of 0.46 and 0.89 eV for nanoparticles of radii 2.0 and 1.5 nm respectively. Polydispersity leads to asymmetric broadening and a marginal shift of peak position.

APPLICATIONS OF CdS NANOCRYSTALS

The application based properties of CdS nanocrystals are as follows:

- 1 When irradiated with light, the conductivity of CdS increases (used as a photo resistor).
- 2 When combined with a p – type semiconductor it forms the core component of a photovoltaic (solar) cell. Moreover, CdS/Cu₂S solar cell was one of the first efficient cells to be reported.
- 3 When fabricated in thin films, it can form transistors.
- 4 When doped with Cu⁺ (“activater”) and Al³⁺ (“coactivater”) CdS shows luminescence under electron beam excitation (cathodoluminescence) and is used as phosphor.
- 5 Both polymorphs are piezoelectric and the hexagonal form is pyroelectric and electroluminescent.
- 6 CdS crystal can act as a solid state laser.
- 7 CdS nanoparticles used as biolabels because they have nanometric dimension, present an important luminescence signal and most important they are functionalized with organic molecules which have functional groups that can attach them to biomolecules or cells.

CONCLUSIONS

Theoretical values of E_g^{nano} still are larger than that of the experimental values. So equation (2) needs to be modified. Since surface to volume ratio is more in nanocrystal that is more atoms are on the surface so strain effect due to intermolecular

attractive forces may be taken into account and an additional term must be subtracted in equation (2).

The experimental results for the blue shift of the PL - spectrum that is well explained by the theoretical observation while broadening of the band edge luminescence essentially arises due to the particle size distribution. In the case of the polydispersed nanoparticles, most of them spend lesser time in the excited states and we know the width ($\text{FWHM} = \Delta\omega$) is inversely proportional to the relaxation time Δt , which may take place through the following modes:

(a) Spin – lattice relaxation

In the case of paramagnetic substance (unpaired electrons), due to larger magnetic moment of electrons, the relaxation is very low that is, Δt is very low during the spin - lattice relaxation, hence the broadening in the spectral lines takes place.

In the case of polydispersed substances, nanoparticles take the form quadrupole and resulting quadrupole moments speed up the spin - lattice relaxation resulting in the widening of the width of the spectral lines.

(b) Spin - spin relaxation

Precession of the magnetic nucleus of the nanoparticles can be resolved into the rotating and static components. The static component of another nucleus causes a slight variation in the effective field of this second nucleus neighboring atoms will have much appreciable effect. So with decreasing size of the nanoparticles, the effect becomes

more pronounced and relaxation becomes faster so the broadening results.

The following points may be considered for further studies of CdS nanoparticles:

- In step (III), there is no fixed optimum time duration in which we get maximum nanoparticles.
- In step (I), if the quantity of CdCl_2 is increased, the time for centrifuge also increases. Is there any relation between the quantity and the time?
- Is optimum time for CdS, ZnS, CdSe, ZnSe and other sample for same quantity the same?
- Same concentration of step (I) for different materials gives same number of nanoparticles or different.

REFERENCES

1. L. E. Brus, *J. Chem. Phys.* 80, 4403 (1984).
2. T. R. Ravindran, Ahilesh K. Arora, B. Balamurugan and B. R. Mehta, *Nanostructured Materials*, Vol.11, No.5, 603 (1999).
3. L. Brus, *J. Phys. Chem.* 90, 2555 (1986).
4. D. J. Norris and M. G. Bawendi, *Phys. Rev. B* 53, 16338 (1995).
5. M. Nirmal, D. J. Norris, M. Kuno, M. G. Bawendi, A. L. Efros and M. Rosen, *Phys. Rev. Lett.* 75, 3728 (1995).
6. Rajeev R. Prabhu and M. Abdul Khadar, Vol. 65, No. 5, P. 801-807, (2005).
7. J. Hasanzadeh and S. Farjami Shayesteh, *Optica Applicata*, Vol. XLI, No.4 (2011).
8. G.A. Martinez- Castanon, J. P. Loyola-Rodriguez, J. F. Reyes-Macias, *Superficies y Vacio* 23 (4), P. 1-4, (2010).
9. K. Manickathai, S. Kasi Viswanathan and M. Alagar, *Indian Journal of Pure & Applied Physics*, Vol. 46, P. 561-564, (2008).
10. M.J. Padwar and S. S. Chaure, Vol. 6, No. 12, P. 689-693, (2009).